ENSYN
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To the California Air Resources Board Co-processing Work Group:

Ensyn Corp would like to formally submit the following response to the information presented during the most recent Co-processing Work Group meeting held at the California Air Resources Board (ARB). We understand that our joint venture partner, Honeywell UOP, will respond under separate cover.

Ensyn's response is divided into two sections. The first part addresses the three formal presentations on ^{14}C radiocarbon biocarbon yield analysis (^{14}C yield methods) that were presented at the ARB Co-processing Work Group meeting on October 19, 2018. These presentations are addressed in the context of FCC biocrude co-processing in FCC (fluid catalytic cracking) refinery unit operations and in the context of standard reliable statistical mass balance methodologies that are routinely used in such operations. Section 1 is primarily a *technica*l response.

The second part, Section 2, is less technical and more qualitative in nature, yet it does relate the conclusions of prior mass balance and ^{14}C technical reports, in summary format, and to the discussion and content presented at the recent ARB Co-processing Work Group meeting It is important to note the above-referenced technical reports were formally submitted by to the California ARB by Ensyn, Tesoro, Honeywell UOP, NREL, Petrobras, Canmet, and other FCC biocrude co-processing stakeholders.

It is also important to note that biofuel/biomass co-processing is a very broad technical category encompassing a vast array of biofuel inputs and petroleum refining unit operation combinations. The response and technical representations contained herein are focused on a very specific subset of co-processing – the co-processing of biocrude (pyrolytic "liquid wood") in an FCC unit, or "FCC biocrude co-processing." The representations and technical opinions referenced have been expressed by both independent entities and interested co-processing stakeholders that are highly credible with impeccable technical credentials. These sources are those that are actually engaged and experienced in FCC biocrude co-processing activities. There is no attempt to extrapolate the expert opinion and technical conclusions relating to FCC biocrude co-processing to other co-processing pathways, particularly where direct experience is lacking.

Robert Graham, Ph.D.
Executive Chairman

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SECTION 1.
Comments on the three formal technical presentations made at the October 19, 2018 ARB Co-processing Work Group meeting.

Presentation 1: "Bio-based Carbon Content Test Method Evaluation" (REG)

Significantly, this is a laboratory-based "doping" study designed simply to determine the biogenic carbon content or percent modern carbon (PMC) of non-coprocessed samples under non-FCC biocrude co-processing conditions. It is based on a prepared sample that is constructed by blending petroleum products with a finished biofuel under laboratory-controlled conditions. The biofuel-petroleum samples have not undergone any chemical processing during their integration and mixing together, and the biofuel is not representative of biomass-derived transportation fuels that are produced in an FCC during thermally and catalytically operating conditions.

This ^{14}C analysis was based simply on the introduction of a renewable diesel in a known petroleum in measured proportions, and the origin and properties of neither the renewable diesel nor the petroleum are identified.

a. No biofuel co-processing steps of any type were undertaken in this study.
b. There is no commercial basis for the study. It is simply a lab-scale preparation of blended samples without any relation to the process conditions, chemical complexity, and proportions of biofuel typically associated with co-processing, particularly FCC biocrude co-processing.
c. On its face, the study bears no relationship to co-processing, co-processing conditions, and co-processing yield structures – the authors do not attempt to make any representations on the applicability of the study and its relationship to co-processing.
d. The study indicates that ^{14}C would be an accurate means of determining carbon in a blended fuel, although ^{14}C is not currently used in any such commercial application. In fact, when questioned, the REG presenter indicated that they did not perform ^{14}C analysis at their facilities or on their fuels.
e. The source of the biofuel used was not identified nor was the method used to produce it, however, the REG presenter did say that it did not come from a REG process.
f. The analysis performed in this study has only established that in cases where biofuel, particularly biodiesel or renewable diesel, is *blended* with petroleum (i.e. not thermally or chemically co-processed) ^{14}C can identify the presence of modern carbon in the blended fuel, and may therefore be useful in this specific circumstance and application.

The lack of correspondence and applicability of the study methods to co-processing, particularly to FCC biocrude co-processing, is even more pronounced when one examines the necessity for corrections and the limits of detection that are evident and must be considered when using the stated ^{14}C methodologies.

a. Corrections:

   I. It is necessary to know or to determine the year atmospheric carbon was fixed in the biomass plant material (this was elaborated on in more detail in the Lawrence Livermore National Laboratory presentation and clearly illustrated some of the problems associated in making this determination with older cellulosic feedstocks). This is rarely known for those cellulosic biomass samples from which the co-processed feedstocks are derived.

   II. A blank correction is necessary to account for the cumulative systematic error. Again, for those feedstocks that are of more recent growth (e.g., oil seeds) this may be less of an issue in the selection of the carbon year. However, for much older cellulosic based feedstocks this procedure is not as straightforward.

b. Limit of detection of 0.4%: In once-through or simple co-processing processes where a single relatively homogeneous biofuel is the input and a single transportation product is the output the limit of detection of 0.4% for ^{14}C methods is not as technically restrictive and onerous. In this case, one could assume from the paper that ^{14}C methods could be applied and would be as equally valid and reliable as standard mass balance methods. However, in processes, such as FCC biocrude co-processing, with numerous product outputs derived from the co-processing of relatively low introductions of non-homogeneous bio-based feedstocks, the level of detection certainly presents an accuracy and reliability issue for ^{14}C methods – most certainly at lower biocrude addition levels in FCC co-processing.

Presentation 2. University of California Davis work

Many of the comments made above in the context of Presentation 1, in reference to the nature of the sample, its preparation, and its lack of relevance to co-processing conditions and biofuel addition rates, also apply to this study.

a. The limit of detection was estimated at approximately 0.5%. Once again, this presents a serious problem whenever the method is applied to the co-processing of low-levels of bio-based materials, particularly when applied to FCC biocrude co-processing.

b. There is a requirement for a “blank” correction. The U.C. Davis work reiterated and emphasized the necessity to include a blank correction. This blank correction was deemed necessary due to the fact that “even small amounts of ^{14}C contamination can cause bias.” Again, given the nature of older cellulosic bio-based feedstocks and indeterminate age distributions, this will present an inherent reliability issue.

Presentation 3. Lawrence Livermore National Laboratory Work

From Ensyn’s perspective, this was a well-delivered presentation that clearly outlines the challenges in analyzing the isotopes of carbon. The sophistication of ^{14}C techniques and the complexities and variables associated with them are clearly expressed in the written and oral presentations. It is stated that few labs, if any, have the sophistication and capabilities of the Lawrence Livermore National Laboratory (LLNL) to account for the complexities and anomalies, particularly in the context of actual refining operations. LLNL was the only presenter to both consider and make reference to refinery operations and the application of ^{14}C methods thereto.

Particularly noted in the presentation, having relevance to actual commercial FCC biocrude co-processing conditions:

a. Bomb pulse of ^{14}C can complicate matters for biomass that is older (especially decades old)

   I. Atmospheric testing of nuclear weapons from 1950-1963 produced a global pulse tracer.

   II. Since all plants are labeled with the ^{14}C content of the atmosphere at the time of synthesis, older cellulosic-based biomass will exhibit traces of the global pulse tracer.

   III. The presenter reiterated in post-Work Group discussions that those woody biomass-based feedstocks or derivatives thereof, which may be older, present complications and difficulties for accurate ^{14}C analysis, especially at low detection levels that are characteristic of FCC biocrude co-processing.

b. Measurement Precision

   I. The final slide in the LLNL presentation confirms that at low renewable feedstock substitution levels, such as in the case in FCC biocrude co-processing, the ratio of modern carbon to total carbon can be extremely low, requiring the detection of less than 1 part PMC in 5 parts per quadrillion total Carbon. This is well below the precision limits for the prescribed ^{14}C methodology, yet is fully and statistically manageable by the statistical mass balance methods that are routinely used in petroleum refineries.

c. Nature and Properties of the Biogenic Sample

   I. LLNL points out that the nature and properties of the samples are important considerations for ^{14}C analytical techniques.

   II. Gas samples, for example, are very difficult to analyze.

   III. Extremely volatile samples are also difficult due to the potential of sample mass loss. This is very relevant in FCC biocrude co-processing operations.

   IV. Specifically, in refinery operations, naphtha (one of the primary products from biocrude during FCC co-processing) can be difficult to accurately analyze via ^{14}C methods because of the volatile nature of many of its constituents.

General Comments Relating to the ARB Co-processing Work Group Presentations and the resultant oral discussions:

a. Notably, two of the three technical presentations given at the ARB Co-processing Work Group were in no way based on, or focused on, actual co-processing samples. They addressed only *neat* (pure) biofuels blended with *neat* petroleum prepared in a laboratory and without any co-processing context or individual analysis of the initial neat samples. It is interesting to note that the leading proponent of ^{14}C analysis is not required to use ^{14}C methods, nor does it recommend the use of ^{14}C methods, to substantiate the amount of biogenic carbon in its commercial biodiesel products, while at the same time recommending that its competitors do so. In fact, REG was asked at the Work Group meeting if it used ^{14}C to measure biogenic carbon in its products and it answered in the negative. Again, the leading proponent of ^{14}C methodologies is advocating for a method that it does not itself use and is attempting to require its application to an area where it does not reliably and accurately apply.

b. Blend ratios in FCC biocrude co-processing are low, typically less than 5% of the total feedstock added to the FCC.

c. There are multiple product streams exiting from the FCC. The renewable carbon in product streams can be below or near ^{14}C methodology detection limit thus creating the potential for false negative outcomes.

d. There will be age variability and other variability of the sourced biomass used to produce the liquid biomass feedstock (i.e., biocrude) that is co-processed in a refinery FCC, potentially leading to difficulties in blank correction requirements.

e. ASTM 6866 currently stipulates reporting ^{14}C results in rounded whole numbers which can drastically swing the results either negatively or positively at the low blend ratios of co-processing in FCC.

SECTION 2.
Specific Comments and Conclusions on FCC Biocrude Co-processing yield methodologies (taking into consideration the technical papers and opinions that have been previously filed with the ARB [https://www.arb.ca.gov/fuels/lcfs/workshops/11092017_ensyn-honeywell.pdf] and also taking into consideration the presentations and discussions at the ARB Co-processing Work Group meeting on October 19, 2018)

1. FCC biocrude co-processing is a particular subset of the broad category of biomass/biofuel co-processing. "FCC biocrude co-processing" refers specifically to the addition of 5% or less biocrude feedstock to petroleum feedstock during the co-processing of biocrude with petroleum in a Fluid Catalytic Cracking (FCC) unit operation in a petroleum refinery. The authors of the this current written response to the California ARB, as well as the FCC biocrude co-processing stakeholders and multiple technical experts who have commented on FCC biocrude co-processing in the public domain (including public filings with the California ARB) are focused on this subset only.

2. Note that these same authors, stakeholders and experts are those who are actually working in the field of FCC biocrude co-processing and have practical hands-on experience in the field, including pilot plant, demonstration and commercial FCC biocrude co-processing trials and analytical methodologies associated with those trials. No attempt is made to comment on, or make recommendations on, other co-processing pathways with which the authors, stakeholders and experts have little or no expertise.

3. The FCC biocrude co-processing experts include those employed by National Laboratories, other independent laboratories, energy technology companies, biofuel companies, and refiners.

4. FCC biocrude co-processing stakeholders and technical experts, as indicated above, have unanimously recommended using only statistical mass balance methodologies to

determine the yields of renewable gasoline and diesel that can be attributed to the addition and presence of biocrude during the FCC biocrude co-processing.

5. More specifically, the Honeywell UOP mass balance methodology ("UOP Honeywell MassBal"), as submitted to the California ARB on three occasions including a formal response to the October 19, 2018 Co-processing Work Group meeting, is recommended for use in FCC biocrude co-processing operations. UOP Honeywell MassBal is the only accurate method, and the only existing reliable method, for determining the yields of renewable gasoline and diesel that can be directly attributed to biocrude in FCC biocrude co-processing operations.

6. Alternative ^{14}C yield methodologies have been proposed by competitors, and by those who are not actively working in the FCC biocrude co-processing field, for application to FCC biocrude co-processing operations. It is interesting to note that those who are proposing that these ^{14}C methodologies be used in FCC biocrude co-processing operations are admittedly not using ^{14}C methods to validate the biocarbon content of their own biofuels or blends that contain them.

7. The application of such alternative ^{14}C yield methodologies to FCC biocrude co-processing have been broadly and unanimously discredited and rejected by a broad array of interested and independent expert entities that are actually working in the FCC biocrude co-processing field. The papers, opinions and letters that express this sentiment are in the public domain and have been filed with the California ARB. Such expert opinions include two National Laboratories (NREL and Canmet), the world's leading petroleum technology company (Honeywell UOP), co-processing technology companies (Ensyn & Envergent), petroleum refining trade associations, refiners (Petrobras, Andeavor and Chevron), etc.

8. Petrobras and NREL conducted the most notable, and the only public domain, results of a FCC biocrude co-processing commercial demonstration trial. Apart from their standard mass balance yield methodology, they attempted an alternative ^{14}C yield methodology and explicitly reported that ^{14}C yield methodologies were not reliable for FCC biocrude co-processing where biocrude addition is less than 5%. At higher addition rates, 10 to 20%, they reported that ^{14}C yield could have some applications. Along with other independent researchers and stakeholders, they concluded that mass balance was the only accurate and reliable method for the determination of renewable gasoline and diesel yields that arise from FCC biocrude co-processing.

9. It is very important to note that Ensyn and its partners and stakeholders have conducted dozens and dozens of FCC biocrude co-processing pilot, demo and commercial trials worldwide. These trials involved a broad array of independent, national and stakeholder laboratories and commercial refiners. At no time was any form of ^{14}C yield

methodology considered, recommended or utilized to determine renewable gasoline and diesel yields. In all cases, the standard "default" yield methodology has been mass balance and results have been accurate and consistent among the various test facilities.

10. To the knowledge of Ensyn, its partners and stakeholders, there is not one instance of any legitimate challenge to the technical integrity, reliability or accuracy of statistical mass balance methodologies (particularly, the Honeywell UOP Massbal yield methodology) when applied to determine the yields of renewable gasoline and diesel attributed to biocrude during FCC biocrude co-processing operations. On the other hand, as already noted, there is essentially a universal rejection (by those technical experts actually working in the field) of the application of ^{14}C methodologies to determine accurate and reliable renewable gasoline and diesel yields from biocrude during FCC biocrude co-processing operations, as defined.

11. The California ARB is strongly urged to retain their draft recommendation that mass balance, the only universally-endorsed methodology, be the primary methodology used to determine renewable gasoline and diesel yields during FCC biocrude co-processing operations. More specifically, it is urged and recommended that the Honeywell UOP Massbal yield methodology be the primary methodology used to determine renewable gasoline and diesel yields during FCC biocrude co-processing operations.